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A General Equation of the Polarographic Wave Applicable to Solvents of Low Dielectric Constant; Effect of Ion-pair Formation on Half-wave Potentials

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An equation of the polarographic wave is derived taking into account possible ion-pair formation involving both the supporting electrolyte salt and the reducible cation. Under conditions such that ion-pair formation is extensive, the half-wave potential is a function of the ion-pair association constants of both the supporting electrolyte and the reducible cation and is a function of supporting electrolyte concentration. Polarographic data obtained in anhydrous ethylenediamine as solvent (dielectric constant = 12.5) substantiate the equation. The equation can be modified easily to include the effects of complex-ion formation as well as ion-pair formation and activity coefficient changes, so that the resulting general equation describes the effects of all principal types of interactions between the supporting electrolyte salt and the reducible cation in any solvent medium.

Introduction

Reversible polarographic waves have been observed in a variety of solvent media with widely varying dielectric constants. In all of these solvent media, and for a number of possible reasons, the half-wave potentials may be expected to vary, more or less, with the concentration of supporting electrolyte. In aqueous solution the effects of ionic strength and supporting electrolyte concentration have been considered by Lingane[1] and by DeFord and Anderson[2] from both theoretical and experimental standpoints. The latter authors observed a fairly large variation in half-wave potential with changing ionic strength. They were able to show that, at least at moderate values of ionic strength, the effect of the ionic atmosphere on the activity coefficient of the reducible cation accounted for most of the observed shift in half-wave potential with changing supporting electrolyte concentration, providing of course that the supporting electrolyte anions did not appreciably complex the reducible cations.

In non-aqueous or mixed aqueous-organic solvent media of lower dielectric constant, ion-pair formation can become important and can actually become the predominant factor affecting the half-wave potential. In fact, Kolthoff and Bruckenstein[3] conclude that in glacial acetic acid, which has a dielectric constant of 6.13, association is so extensive that the ionic atmosphere is negligible and activity coefficients of the free ions may not be greatly different from unity.

It is the purpose of this paper to derive the equation of the polarographic wave which would be applicable to solvents of lower dielectric constant and which would express the effect, on the half-wave potential, of ion-pair formation involving the reducible cation and the supporting electrolyte and then to test the equation experimentally, in so far as possible. The equation derived will be for the case of the reversible reduction to the metallic state of solvated cations of metals that are soluble in mercury.

Discussion

The equation of the polarographic wave applicable to solvents of low dielectric constant, where ion-pair formation occurs, can be derived in a manner analogous to the derivation of the equation for the reduction of a metal ion in the presence of complexing ligands in aqueous solution.[4a,5] Assume that the reducible cation, M^{+n}, is present at a total *stoichiometric* concentration, C_M, in a solution which contains a uni-univalent supporting elec-

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[1] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

[2] D. D. DeFord and D. L. Anderson, *ibid.*, **72**, 3918 (1950).

[3] I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 1 (1956). In this connection see also C. A. Kraus, *J. Chem. Ed.*, **35**, 324 (1958).

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, (a) Chapt. XII, (b) Chapt. XI.

[5] D. D. DeFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

trolyte salt, SX, at a much higher *stoichiometric* concentration, C_{SX}. (Note that the anion, X^-, of the supporting electrolyte salt predominates in solution regardless of the anion added with the reducible metal ion. The latter anion will be disregarded in the ion-pair association equilibria.) In the equations below, K_{SX} is the ion-pair association constant of the supporting electrolyte salt and α is its degree of association (concentration basis). All ion pairs are enclosed in braces and the square brackets denote activities. Thus

$$K_{SX} = \frac{[\{S^+, X^-\}]}{[S^+][X^-]} = \frac{[\{S^+, X^-\}]}{[X^-]^2} \quad (1) \text{ and}$$

$$[X^-]^n = [\{S^+, X^-\}]^{n/2}/K_{SX}{}^{n/2} \qquad (2)$$

If f_{SX} is the activity coefficient of the associated ion pairs, $\{S^+, X^-\}$, then in terms of α

$$[\{S^+, X^-\}]/f_{SX} = \alpha C_{SX} \text{ and } [X^-]/f_X = (1 - \alpha)C_{SX}$$

Thus

$$K_{SX} = \alpha f_{SX}/(1 - \alpha)^2 C_{SX} f_X{}^2 \qquad (3)$$

The value of α can be obtained exactly (in principle) by solution of the quadratic equation 3. However, if f_{SX} is assumed to be near unity and the product $C_{SX}K_{SX}f_X{}^2 \geqq$ *ca.* 10, then to a good approximation $1 - \alpha = 1/C_{SX}{}^{1/2}K_{SX}{}^{1/2}f_X$ and $[X^-] = C_{SX}{}^{1/2}/K_{SX}{}^{1/2}$ (4). The approximation for α is accurate to about 5% at $\alpha = 0.7$ and improves rapidly for larger values of α, *i.e.*, for increasing association of the supporting electrolyte.

The step-wise ion-pair association equilibria involving the reducible metal ion, M^{+n}, and the predominant anion, X^-, are as follows. (Charges are omitted in the k_j expressions for simplicity.)

$$M^{+n} + X^- \rightleftharpoons \{M^{+n}, X^-\}^{+n-1} \quad k_1 = \frac{[\{M^{+n}, X^-\}]}{[M^{+n}][X^-]}$$

$$\{M^{+n}, X^-\}^{+n-1} + X^- \rightleftharpoons \{M^{+n}, 2X^-\}^{+n-2}$$

$$k_2 = \frac{[\{M^{+n}, 2X^-\}]}{[\{M^{+n}, X^-\}][X^-]}$$

Finally, the last association step results in the formation of a neutral species, *i.e.*

$$\{M^{+n}, (n - 1)X^-\}^+ + X^- \rightleftharpoons \{M^{+n}, nX^-\}^0$$

$$k_n = \frac{[\{M^{+n}, nX^-\}]}{[\{M^{+n}, (n - 1)X\}][X^-]} = \frac{[\{M^{+n}, nX^-\}]}{k_1k_2\cdots k_{n-1}[M^{+n}][X^-]^n} \qquad (5)$$

(The effects of higher aggregates—triple, quadruple ions and polymers—will not be considered in this derivation.)

If the total stoichiometric concentration of metal ion present in all forms is C_M, and the concentration of each individual species, C_{MXj}, is $[\{M^{+n}, jX^-\}]/f_{MXj}$, *then*

$$C_M = [M^{+n}]/f_M + [\{M^{+n}, X^-\}]/f_{MX} + [\{M^{+n}, 2X^-\}]/f_{MX_2} + \cdots + [\{M^{+n}, nX^-\}]/f_{MX_n}$$

$$C_M = [M^{+n}]\{1/f_M + k_1[X^-]/f_{MX} + k_1k_2[X^-]^2/f_{MX_2} + \cdots + k_1k_2\cdots k_n[X^-]^n/f_{MX_n}\} \qquad (6)$$

Writing $k_1 = K_1$, $k_1k_2\cdots k_n = K_n$ ($K_0 = 1$), then equation 6 can be rewritten

$$C_M = [M^{+n}] \sum_{j=0}^{n} K_j [X^-]^j/f_{MXj} \qquad (7)$$

Substituting $[X^-] = (1 - \alpha)C_{SX}f_X$ into equation 7

$$C_M = [M^{+n}] \sum_{j=0}^{n} K_j(1 - \alpha)^j C_{SX}{}^j f_X{}^j/f_{MXj} \qquad (8)$$

Or, if the approximation in equation 4, valid for $\alpha >$ *ca.* 0.7, is introduced

$$C_M = [M^{+n}] \sum_{j=0}^{n} K_j C_{SX}{}^{j/2}/K_{SX}{}^{j/2} f_{MXj} \qquad (9)$$

The equation expressing the potential of a dropping mercury electrode (for the case being considered) may be written[4b,5]

$$E_{d.e.} = E_a{}^{0\prime} - E_L - \frac{RT}{nF} \ln \frac{C_a{}^0 f_a}{[M^{+n}]^0} \qquad (10)$$

where $E_a{}^{0\prime} = E_a{}^0 + (RT/nF)\, ln\, a_{Hg}$ and the terms $C_a{}^0$ and $[M^{+n}]^0$ are the concentration of the amalgam and the activity of the metal ion, respectively, at the surface of the mercury drop. If an external reference electrode is used, the term $-E_L$ may be included to represent the liquid junction potential. However, this term is not carried along in the subsequent equations. Other symbols have their usual significance.[4b] Equation 8 can be written to apply to the conditions existing at the surface of the mercury drop, *i.e.*

$$[M^{+n}]^0 = C_M{}^0 \Big/ \sum_{j=0}^{n} K_j (1 - \alpha)^j (C_{SX}{}^0)^j f_X{}^j/f_{MXj}$$

Substitution into equation 10 gives

$$E_{d.e.} = E_a{}^{0\prime} - \frac{RT}{nF} \ln \frac{C_a{}^0 f_a}{C_M{}^0} \sum_{j=0}^{n} K_j(1 - \alpha)^j C_{SX}{}^j f_X{}^j/f_{MXj} \qquad (11)$$

(In equation 11 the concentration of supporting electrolyte in the bulk of the solution, C_{SX}, is considered to be equal to that at the electrode surface, $C_{SX}{}^0$, because of its presence in large excess.) Alternatively, substitution for $[M^{+n}]^0$ from equation 9 gives for the limiting case of predominant ion-pair association involving the supporting electrolyte

$$E_{d.e.} = E_a{}^{0\prime} - \frac{RT}{nF} \ln \frac{C_a{}^0 f_a}{C_M{}^0} \sum_{j=0}^{n} K_j C_{SX}{}^{j/2}/K_{SX}{}^{j/2} f_{MXj} \qquad (12)$$

DeFord and Hume[5] have derived expressions relating polarographic current to the concentrations of the co-existing, stepwise complexes of a reducible cation. Using analogous relations for the stepwise ion-paired species involving the metal cation, M^{+n}, one can write

$$i = k \sum_{j=0}^{n} I_{MXj}(C_{MXj} - C_{MXj}{}^0)$$

and

$$i_d = kI_{C_M} \sum_{j=0}^{n} C_{MXj}$$

also

$$i = k'I_a C_a{}^0$$

Thus

$$C_M{}^0 = \sum_{j=0}^{n} C_{MXj}{}^0 = \frac{i_d - i}{kI_{C_M}} \qquad (13)$$

and

$$C_a{}^0 = i/k'I_a \qquad (14)$$

In the above equations I_{MXj} is the diffusion current constant ($605\, nD_{MXj}{}^{1/2}$) for each MXj species, I_{C_M} is the over-all, measurable diffusion current constant for a given solution containing any one or all of the possible species involving the reducible metal ion, and I_a is the constant for the metal in the amalgam. Also, k and k' are proportionality constants which may be assumed to be equal.[5]

Inserting these last two equations into equation 11 gives the complete expression for the potential of the dropping mercury electrode, applicable to any solvent.

$$E_{d.e.} = E_a^{0\prime} - \frac{RT}{nF} \ln \frac{if_a I_{C_M}}{(i_d - i)I_a} \sum_{j=0}^{n} K_j (1 - \alpha)^j C_{SX}^j f_X^j / f_{MX_j} \quad (15)$$

Separating the various terms in equation 15, the usual equation describing the shape of the reversible polarographic current–voltage wave is obtained, *i.e.*

$$E_{d.e.} = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \quad (16)$$

where, however, the half-wave potential is now given by the expression

$$E_{1/2} = E_a^{0\prime} - \frac{RT}{nF} \ln \frac{f_a I_{CM}}{I_a} - \frac{RT}{nF} \ln \sum_{j=0}^{n} K_j (1 - \alpha)^j C_{SX}^j f_X^j / f_{MX_j} \quad (17)$$

A simpler expression for $E_{1/2}$ is obtained if equations 13 and 14 are combined with equation 12, *i.e.*

$$E_{1/2} = E_a^{0\prime} - \frac{RT}{nF} \ln \frac{f_a I_{CM}}{I_a} - \frac{RT}{nF} \ln \sum_{j=0} \frac{K_j C_{SX}^{j/2}}{f_{MX_j} K_{SX}^{j/2}} \quad (18)$$

If the dielectric constant of the solvent is sufficiently low (and the concentrations sufficiently high), so that both the supporting electrolyte and reducible cation are present predominantly as the neutral species, *i.e.* $\{S^+, X^-\}$ and $\{M^{+n}, nX^-\}$, then equation 18 becomes at 25°

$$E_{1/2} = E_a^{0\prime} - \frac{0.059}{n} \log \frac{f_a}{f_{M_{X_n}}} - \frac{0.059}{n} \log \frac{I_{CM}}{I_a} - \frac{0.059}{n} \log \frac{K_n}{K_{SX}^{n/2}} - 0.03 \log C_{SX} \quad (19)$$

In equation 19 $E_a^{0\prime}$ is the "standard" potential of the metal amalgam electrode in the particular solvent medium used *versus* some arbitrarily selected reference electrode. (A liquid junction potential is implicit in the equation if an external reference electrode is used, which is the usual case.)

The term involving activity coefficients will likely have to be neglected, since few such activity coefficients are presently available for non-aqueous or mixed aqueous solvent systems. However, the error introduced may not be large because the ratio of the coefficients is involved. The term containing the diffusion current constants can be evaluated (in principle) from polarographic data. If the neutral ion-paired species predominates, the value of $I_{CM}/I_a = (D_{MXn}/D_a)^{1/2}$

The term $(0.059/n)\log K_n/K_{SX}^{n/2}$ contains the effects of all the ion-pair association constants ($K_n = k_1 k_2 \cdots k_n$). The ion-pair association constant of the supporting electrolyte is in the denominator, and the $E_{1/2}$ would shift in the positive direction with increasing size of K_{SX}. This shift occurs because as the value of K_{SX} increases less supporting electrolyte would dissociate and fewer anions would be available to form ion-pair "complexes" with the reducible cation. On the other hand, large values for the stepwise ion-pair association constants of the reducible ion, M^{+n}, would shift the $E_{1/2}$ in the negative direction, as might be expected in analogy to complex formation.

If both the supporting electrolyte cation and the reducible ion are univalent, the ion-pair association term reduces to $-0.059 \log k_1/K_{SX}^{1/2}$; and if the constants for these univalent cations are approximately equal, this term becomes $-0.03 \log k_1$. If the reducible ion is divalent, the term is $-(0.059/2) \log k_1 k_2/K_{SX}$.

The last term in equation 19 gives the effect of the supporting electrolyte concentration on the half-wave potential. This term is *independent of the charge* of the reducible ion for the case being considered, *i.e.*, reduction to the amalgam, and for any given metal ion the $E_{1/2}$ should shift 30 millivolts in the negative direction for a ten-fold increase in supporting electrolyte concentration. This theoretical shift should occur only under conditions such that the reducible ion and the supporting electrolyte are both largely present as associated, uncharged species.

If it were possible to obtain by direct measurement or by extrapolation the $E_{1/2}$ of a cation at a sufficiently low concentration of the cation so that ion-pair formation of the reducible ion becomes negligible, then this limiting value of the $E_{1/2}$ may be considered that of the simple, solvated cation in the solvent medium being used and is given by equation 20[4b] in which the subscript M refers to the simple, solvated metal ion.

$$(E_{1/2})_M = E_a^{0\prime} - \frac{RT}{nF} \ln \frac{I_M f_a}{I_a f_M} \quad (20)$$

Combination of equations 19 and 20 gives an expression for the shift in half-wave potential due to ion-pair formation involving the reducible cation and also the supporting electrolyte salt, *i.e.*

$$(E_{1/2})_M - (E_{1/2})_{MX_n} = \frac{0.059}{n} \log \frac{f_M}{f_{MX_n}} + \frac{0.059}{n} \log \frac{I_{C_M}}{I_M} + \frac{0.059}{n} \log \frac{K_n}{K_{SX}^{n/2}} + 0.03 \log C_{SX} \quad (21)$$

Equation 21 can be used to evaluate the ratio of the ion-pair formation constant of the supporting electrolyte to the *over-all* ionic association constant of the cation ($K_n = K_{MX_n}$), if $(E_{1/2})_{MX_n}$ is taken from a concentration region where ion-pair formation is essentially complete.

If K_{SX} for the supporting electrolyte were known, so that α or $[X^-]$ could be calculated at any given concentration, C_{SX}, of the supporting electrolyte, then it should be possible to evaluate the stepwise ion-pair formation constants, $k_1, k_2 \cdots k_n$, of the cation M^{+n} with the anion X^- using a procedure analogous to that used by DeFord and Hume for evaluating stepwise formation constants of complex ions.[5]

It is interesting to notice that if j in equation 15 is not limited by n, the charge of the reducible cation, but is allowed to expand up to the maximum coördination number of the cation, N, then

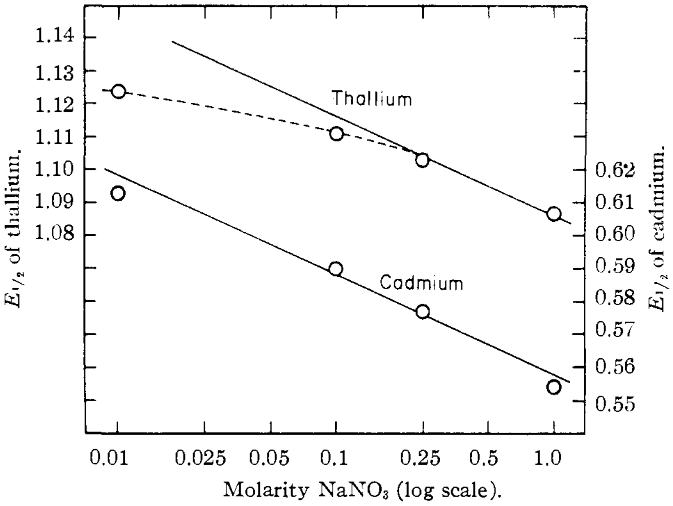

Fig. 1.—Effect of supporting electrolyte concentration (sodium nitrate) on the half-wave potentials of thallium and cadmium in anhydrous ethylenediamine as solvent (potentials measured *vs.* the zinc amalgam–zinc chloride reference electrode). Solid lines are drawn with the theoretical slope of 0.030 v.

the equation describes all principal interactions between the reducible ion and the supporting electrolyte, *i.e.*, complex formation as well as ion-pair formation and activity coefficient changes. This general polarographic equation, *applicable to all solvent media*, is

$$E_{\mathrm{d.e.}} = E_{\mathrm{a}}{}^{0'} - \frac{RT}{nF} \ln \frac{i f_{\mathrm{a}} I_{\mathrm{CM_C}}}{(i_{\mathrm{d}} - i) I_{\mathrm{a}}} \sum_{j=0}^{\mathrm{N}} K_{\mathrm{j}} (1 - \alpha)^{i} C_{\mathrm{SX}}{}^{i} f_{\mathrm{X}}{}^{i} / f_{\mathrm{MX_j}} \quad (22)$$

This raises the problem of distinguishing between ion-pair formation and the formation of lower coördination complexes. The experimental measurements would reflect the combined effects, but the magnitudes of the constants involved would indicate the relative importance of the two types of interactions. For example, in a solvent of high dielectric constant, a strong interaction between oppositely charged species could occur only *via* coördination. In solvents of low dielectric constant, ion pair formation would become important but to a rather predictable extent.[6] It would then depend upon the relative coördinating ability of the solvent molecules compared to that of the anion whether ion-pair formation or complexing would predominate. In liquid ammonia or ethylenediamine, for example, ion-pair formation would be expected to be far more important than complex formation if the anions present were weakly coördinating, such as chloride or nitrate. If complex formation between the supporting electrolyte anion and the reducible cation can occur while ion-pair formation involving the supporting electrolyte cannot occur, *i.e.*, $\alpha = 0$ and $C_{\mathrm{SX}} = C_{\mathrm{X^-}}$, then equation 22 reduces to a form identical with the general equation for complex formation given by DeFord and Hume[5] for aqueous solutions.

Results

At present, data are not available in the literature for any low dielectric constant solvent medium which can be used to test equations 17, 18 or 19 adequately. Usually only one concentration of a given supporting electrolyte salt is used. However, recent polarographic studies carried out in anhydrous ethylenediamine (dielectric constant = 12.5) as solvent in this Laboratory[7] provide data which appear to support the above equations. These studies show that for several different reducible cations, a change in supporting electrolyte concentration from 0.25 *M* to 0.10 *M* produces a consistent change in $E_{1/2}$ of about ten millivolts, regardless of whether the supporting electrolyte is lithium chloride or sodium nitrate. (To test the effect of changing supporting electrolyte concentration on $E_{1/2}$ further, additional measurements have now been carried out over a wider range of supporting electrolyte concentrations and are reported below.) Furthermore, these studies show that half-wave potentials of cations in ethylenediamine change appreciably when the identity of the supporting electrolyte salt is changed. For example, the $E_{1/2}$ values of thallium, when measured in 0.1 *M* solutions of tetra-*n*-butylammonium iodide, sodium nitrate and lithium chloride, are 1.082, 1.113 and 1.048 volts, respectively, while the $E_{1/2}$ values of cadmium in the same three solutions are 0.578, 0.590 and 0.541 volts, respectively, *versus* the zinc amalgam–zinc chloride reference electrode. These changes in $E_{1/2}$ evidently can be large compared to those observed with changing supporting electrolyte concentration and must be related to appreciable differences in the magnitudes of the ion-pair association constants of the reducible cations with the different anions and to changes in the association constants for the various supporting electrolyte salts.

The experimentally measured half-wave potentials of cadmium and thallium in ethylenediamine at several different concentrations of sodium nitrate as supporting electrolyte are as follows: For cadmium in 1.0, 0.25, 0.10, 0.010 *M* $NaNO_3$, $E_{1/2} = +0.554$, 0.577, 0.590, 0.613 volts, respectively, *versus* the zinc amalgam–zinc chloride reference electrode. For thallium, at the same concentrations of sodium nitrate, $E_{1/2} = +1.087$, 1.103, 1.111 and 1.124 volts, respectively. These $E_{1/2}$ values are averages of at least six polarograms run on at least two different solutions. The replicate values at a given concentration of supporting electrolyte showed a maximum variation of about two millivolts from the means. Corrections for changes in diffusion current constants were made according to equation 19; however, these amounted to only several millivolts at the extreme and neither the data nor the corrections are therefore included here.

The measured $E_{1/2}$ values are plotted *versus* the logarithm of supporting electrolyte concentration, log C_{SX}, in Fig. 1. The straight lines are drawn with the theoretical slope of 0.030 volt, as predicted by equation 19.

The data points show that the half-wave potential of cadmium does exhibit the theoretical dependence upon supporting electrolyte concentra-

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[6] C. A. Kraus, *J. Chem. Ed.*, **35**, 324 (1958).

[7] R. E. Bayer, Ph.D. Thesis, Indiana University, 1959. (This work will be reported more completely in subsequent papers.)

tion in the concentration region of 0.01 to 1 M sodium nitrate in ethylenediamine and a cadmium ion concentration of 3×10^{-4} M. The data for the singly charged thallous ion at a concentration of 3×10^{-4} M follow the theoretical slope above about 0.2 M sodium nitrate but fall considerably below the expected change at lower concentrations of sodium nitrate. Apparently, ion-pair association of Tl^+ with NO_3^- is predominant only at the higher concentrations of sodium nitrate, but at lower concentrations thallous ion is increasingly dissociated. If the reducible species were essentially completely dissociated, then the $E_{1/2}$ would change comparatively little with supporting electrolyte concentration and the plot would be approximately horizontal, as is the case in aqueous solution if the anion of the supporting electrolyte does not form complexes with the reducible ion. The greater degree of ion-pair association of Cd^{++} than Tl^+ in the more dilute sodium nitrate solutions is understandable on the basis of its higher charge and smaller size.

Experimental

The general experimental procedures used to study the polarographic characteristics of metal ions in ethylenediamine have been described previously.[7,8] The ethylenediamine used was dried by refluxing over sodium and then distilled. Sodium nitrate, reagent grade and vacuum dried, was used as supporting electrolyte at concentrations of 1.0, 0.25, 0.10 and 0.010 molar. The chlorides of cadmium and thallium were used to supply these cations at concentrations of about 3×10^{-4} M.

The polarograms were recorded at 25° using a Sargent Model XXI Polarograph and a two-compartment, demountable H-type cell. The cell compartments were separated by a 25 mm. diameter, fine sintered-glass disk. One compartment contained a reference electrode composed of saturated zinc amalgam in contact with ethylenediamine containing 0.25 M LiCl and saturated with respect to zinc chloride.[7] The potential of the dropping mercury electrode was varied with respect to this zinc reference electrode. (The potential of this zinc reference electrode has been found in this Laboratory to be −1.226 volts *vs.* the mercury pool in ethylenediamine containing 0.25 M LiCl and −1.17 volts *versus* the pool in ethylenediamine containing 0.25 M $NaNO_3$.)

Resistances of all solutions were measured with a Serfass conductivity bridge and the half-wave potentials corrected for iR drops. Approximate resistances for the 1.0, 0.25, 0.1 and 0.01 M $NaNO_3$ solutions (in ethylenediamine) were, respectively, 1800, 3000, 6000 and 35,000 ohms.

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Bloomington, Indiana

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[Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute]

Polarographic Determination of Formation Constants of Complex Ions in Fused $LiNO_3$–KNO_3

By Joe H. Christie and Robert A. Osteryoung

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A polarographic study of the chloro-complexes of Pb(II), Cd(II) and Ni(II) has been made with the dropping mercury electrode in a fused $LiNO_3$–KNO_3 mixture at 180°. Respectively, 3, 4 and 2 chloro-complexes were found for these ions yielding these formation constants: Pb(II), $K_1 = 42$, $K_2 = 3$; Cd(II), $K_1 = 200$, $K_2 = 15$, $K_3 = 40$, $K_4 = 5$; Ni(II), $K_1 = 26$, $K_2 = 2$, $K_3 = 10$. The results are compared with other available data.

Introduction

The feasibility of using the dropping mercury electrode (d.m.e.) in fused nitrate melts was demonstrated several years ago by Steinberg and Nachtrieb.[1] Their work indicated that in sufficiently low melting systems the d.m.e. could be utilized in much the same way that it is in aqueous solutions. One use of the polarographic technique in aqueous solutions has been to study complex ions; in certain instances, formation constants for complex ionic species may be determined.[2]

The existence of complex ions in fused salts has been demonstrated, most recently by Gruen[3] and Van Norman,[4] and data on the formation constants for various species have been obtained.[5–8]

It appears that the metal halide complex ions formed in fused salts are characterized by rather weak formation constants. An aqueous polarographic technique for the study of such complexes was derived by DeFord and Hume.[9] The present work is an attempt to apply this method to the determination of formation constants of metal halide complexes in a $LiNO_3$–KNO_3 fused salt system.

Experimental

Reagent grade chemicals were used in all cases. The $LiNO_3$–KNO_3 eutectic system (38.56 mole % $LiNO_3$, m.p. 139°)[10] was prepared from vacuum-oven dried material. In all cases the eutectic material was mixed, fused and filtered through a fine sintered glass frit. Metal ions were added to this mixture as the metal nitrates dried under vacuum at 100°. Additions of chloride were made to the

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